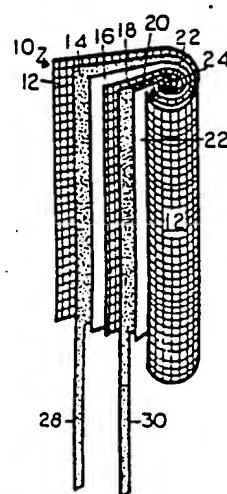


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(54) Title: CHROMATOGRAPHY SYSTEM WITH FLOW-THROUGH CAPACITOR AND METHOD



(57) Abstract

A controlled charge chromatography column (34) with a flow-through capacitor (10) for the purification of a fluid, which column (34) comprises an inlet (40) for the introduction of a fluid to be purified and an outlet (42) for the discharge of the purified fluid, and a flow-through capacitor (10) disposed within the column (34) between the inlet (40) and the outlet (42). The flow-through capacitor (10) comprises a plurality of spirally wound or stacked washer layers (12, 14, 16, 18, 20, 22, 112, 116, 120) to include a first electrically conductive backing layer (14, 20, 116), such as of graphite, and a first high surface area conductive layer (16, 22, 120) secured to the backing layer, such as composed of porous carbon fibers and a non-conductive, porous spacer layer (12, 18, 112) to electrically insulate the backing and conductive layer (14, 16, 20, 22, 116, 120) and to permit the flow of fluid therethrough. The flow-through capacitor (10) is connected to a DC power source (58) to charge the respective conductive layers (14, 16, 20, 22, 116, 120) with different polarities whereby a fluid through the column is purified by the electrically conductive stationary phase (16, 22, 120) and the material is retained onto the high surface area layer (16, 22, 120).

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DESCRIPTION

Chromatography System with
Flow-Through Capacitor and Method

Background of the Invention

5 Chromatographic columns, particularly liquid chromatographic columns, have provided for the employment of an electrically conductive, stationary solid phase, and the preferential interaction of solutes in a fluid to be chromatographically separated with the solid, 10 stationary phase, such as set forth in "Electrically Conductive Stationary Phases for HPLC"¹ issued by Barbara Bassler and Richard Hartwick, Abstract from the AICHE Meeting, San Francisco, California, November 5-10, 1989, and in "Electrochromatography - A Preliminary Study 15 of the Effect of Applied Potential On A Carbonaceous Chromatographic Column"², by Robert Antrim, Robert Scherrer and Alexander Yacynych, Anal. Chim. Acta., 164 (1984) 283. The above references describe an electron rich, porous, graphitic, carbon, stationary phase to 20 act as a controlled potential surface to affect the resolution of solutes to be chromatographed in both polar and non-polar solvents. In such chromatographic columns as HPLC, the conductive packing is employed as one electrode and the surrounding metal tube of the 25 column as the other electrode. These columns do not act as capacitors, since the voltage drop is generally entirely across the metal tube and insignificant across the claimed controlled potential surface to be modulated, so that little electrostatic absorption occurs.

30 In addition, electrically conductive stationary phases have been employed to deposit and strip solutes via electrolysis, see for example, "Continuous Quantitative Electrolysis"³, W.J. Blaedel and J. H. Strohl, Anal. Chem., Vol. 36, No. 7, June, 1964; "A 35 Packed Graphite Cell For Thin Layer Electrochemistry"⁴,

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John Strohl and Thomas Polutanovich, Analytical Letters, 2(8), pp. 423-431 (1969); "Electrolytic Chromatography and Coulometric Detection With the Column Electrode"⁵, Taitiro Fujinaga, Pure Applied Chemistry, 25 (1971) 5 pp. 709-726; and "Modified Graphites for Chelation and Ion Exchange"⁶, James Hern and John H. Strohl, Analytical Chemistry, Vol. 50, No. 14, December, 1978. In addition, capacitance techniques have been employed for the absorption of blood proteins on metals, as set forth by G. Stoner and S. Srinivasan, "Absorbtion of 10 Blood Proteins on Metals Using Capacitance Techniques"⁷, Journal of Physical Chemistry, Vol. 74, No. 5, pp. 1088-1094, March 5, 1970. While electrolysis devices have been used to purify solutions, the devices affect 15 purification by deposition and stripping electrochemically the material and not by electrostatic absorption.

U.S. Patent 4,769,191, issued September 6, 1988, describes an anode electrode of an electrolytic capacitor having a biochemically active layer embedded in the 20 pores of the electrodes and that the electrodes change electrical properties by the presence of the chemical layers. This patent discloses using a biochemical layer and wherein analyte molecules replace other molecules from the biochemically active layer to effect the change 25 in the dielectric properties of the electrodes, and this charge is employed to measure the concentration of analyte molecules.

None of the above prior art references describe 30 a device which affects absorption or resolution of solutes to be chromatographed via a high capacitance, combined with a flow-through configuration to allow the capacitor to function as a chromatographic system. It is desirable to provide for controlled charge chromatography system and method which employs a flow-through capacitor of 35 high surface area material for both anode and cathode, to provide for a high efficiency, effective purifying system to modulate the absorption and/or resolution of ions and non-ionic solutes in polar and non-polar solvents.

Summary of the Invention

The present invention relates to a flow-through capacitor and a controlled charge purification chromatography system and method, and more particularly relates to a chromatography system and method employing 5 a flow-through capacitor of high electrical capacitance and high surface area absorption capacity.

A controlled charge chromatography system and method has been discovered which provides for the purification of solutes particularly in liquids containing both 10 non-polar and polar materials, and which column comprises a column having an inlet for the introduction of the fluid to be purified and an outlet for the discharge of the purified fluid and one or more concentrated ionic materials. The controlled charge chromatographic column 15 would also include a flow-through capacitor means disposed within the column between the inlet and the outlet so as to permit the flow of the fluid through the flow-through capacitor means, with the flow-through capacitor means adapted to be connected to a DC power source to place charges on the film or layers in the 20 capacitor. The flow-through capacitor may comprise a wide variety of configurations, such as for example a spirally wound capacitor. Such a spirally wound, flow-through capacitor would comprise a plurality of 25 spaced apart layers with the layers generally axially aligned with the axis of the column, and the layers including a first non-conductive, porous spacer layer to define a flow channel to permit the flow of the feed fluid therethrough. For example, the spacer material 30 may comprise a porous, inert-type material, such as woven, open space, synthetic material, such as nylon or fiberglass screen-like spacing material. A first electrically conductive backing layer may be composed of any electrically conductive material, such as a metal 35 film for example of aluminum and/or more particularly of electrically conductive graphite. A first high surface area conductive layer material is secured or placed

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adjacent to the electrically conductive backing layer providing a very high surface area by virtue of a highly porous structure, and more particularly would comprise, for example, a compressed, activated carbon which is 5 porous, or even more particularly, an activated carbon woven fibrous layer. The conductive layer may for example be wound in a spiral formation with the porous spacer material between the respective layers with six layers wound so as to provide for separate and opposite charges 10 on two separate spirally wound backing layers.

Electrical leads may be connected to the first and second electrically conductive backing layers to a DC power source so that layers may be formed integrally with the backing layers. Generally, the flow-through 15 capacitor may be prepared in spiral wound form by winding the respective layers about a central hollow perforated tube from inside to outside composed of a spacer layer, a backing layer, a high surface layer, a spacer layer, a backing layer and a high surface layer about a central 20 plastic tube containing perforations therein and then sealed at the end by a resin, such as a thermoset epoxy resin, so as to provide for the introduction of the fluid material through the side of the spirally wound device, through the successive layers, and the purified 25 fluid and the one or more ionic materials concentrated by the flow-through capacitor to be discharged from the other end of the central tube.

The controlled charge ionic purification chromatography system would thus include the 30 chromatographic column containing the flow-through capacitor with a source of fluid, such as a liquid containing ionic materials, a pump means to pump or otherwise introduce the liquid material into the inlet of the chromatographic column, the column typically 35 containing a cartridge-type flow-through capacitor, with the leads of the flow-through capacitor extending out of the column and secured to a DC power source, optionally to a logic device to program voltage on/off

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cycles, voltage gradients and reversal of polarity and otherwise to control electrically the capacitor and wherein the system also includes a collection disposed adjacent the outlet of the column whereby the purified material or the various eluting, concentrated ionic materials may be separately collected.

The method of the invention comprises flowing a fluid containing ionic material, either polar or non-polar solvents, through a flow-through capacitor in which the capacitor is a high capacitance, for example, over 1000 farads capacitance, and further which includes a high surface area conductive layer secured to a backing and separated by a spacing layer from the adjacent high surface area layer and backing so as to increase the retention capacity and electrical capacitance of the capacitor. The charge on the capacitor is controlled so as to attract and hold charged molecules in the fluid by virtue of the charge-holding ability implicit in the capacitance of the capacitor thereby providing for a method of purifying and/or analyzing charged molecules, for example, in a solution by modifying the concentration of the fluid as it passes through the flow-through capacitor.

The flow-through capacitor of the invention may be employed in various designs provided that the solution can flow-through or across the charged metal plates or layers, or ionic plates in the case of electrolytic capacitors, wherein the flow-through capacitor comprises a porous spacer layer to permit the flow of the fluid, an electrically conductive layer and a high surface area electrically conductive layer adjacent or in electrical communication with the backing layer. The flow-through capacitor may comprise a film capacitor wherein the fluid is passed between a pair of metal electrodes having an insulating, dielectric film passed between the electrodes. Some of the film-type capacitors provide for a low capacitance which may be useful for analytical purposes where small amounts of analyte is

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desired. However, such film capacitors have an inherently low capacitance, and therefore, a low charge holding ability. Electrolytic capacitors may also be employed and employ certain metals, such as aluminum and tantalum, which metals tend to form oxide layers which adhere tightly to the metal and which are also good insulators and constitute very thin insulating layers. The capacitance increases with the thinness of dielectric layers. Therefore, these thin oxide layers provide exceptional capacitance. In electrolytic capacitors one of the two metal plates typical of other capacitors has been replaced by an ionic solution which forms intimate contact with the oxide and reacts with the metal to form the oxide itself. Electrolytic capacitors typically use aluminum or tantalum. Aluminum tends to be soluble outside of a narrow pH frame and is readily attacked by halides and therefore is easily corroded, but its cost is low, while tantalum has a non-soluble oxide layer which is stable over a broad pH range and is also immune to corrosion. Hence, the electrolytic capacitors have a relatively high capacitance. However, the amount of capacitance needed to purify even a dilute solution is extremely large, therefore electrolytic capacitors define typical uses for purifying high purity water or protein purification where the feed stream is relatively dilute with the ionic concentrations.

The flow-through, double layer capacitor of the invention avoids the problems associated with typical thin film or electrolytic capacitors, since capacitance is inversely proportioned to the dielectric thickness and directly proportioned to electrode surface area. The flow-through capacitor of the invention employs a conductive layer with a high surface area electrically conductive material layer. In one preferred embodiment, the high surface electrically conductive layer may comprise a porous carbon fiber layer typically a porous, woven, flexible fiber cloth layer in contact with an electrically conductive backing layer, and more

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particularly of a flexible graphite layer which is highly electrically conductive. The high surface area electrically conductive layer may also comprise palladium or platinum black. Activated carbon may also be employed; 5 however, in granular form, activated carbon is not a good electrical conductor unless it is in a compressed, porous form; however, compressing reduces the porosity.

One preferred embodiment of the invention comprises an active carbon fiber woven layer which provides for 10 electrical conductivity and high porosity, although any other material which is highly electrically conductive and which has micropores can be employed for the high surface active area. For example, capacitors made with Toyobo Co. activated carbon KF cloth have 1000X the 15 charge delivery as electrolytics (see "KF for Electro Double Layer Capacitors"⁹, Toyobo Co. Bulletin, PCF 110).

For example, one material which may be employed as the high surface area layer comprises a material 20 known as azite, a black ceramic-like substance, which is highly porous and very strong and yet electrically conductive and is composed of a synthetic carbon polymer whose structure is flat with holes (pores) (see Science¹⁰, January 12, 1990). In addition, it may be desirable 25 to provide for a chemical modification of the high surface area electrically conductive layer by the employment of adsorbing molecules thereon to alter the electrical characteristics, such as for example, adsorbing an aromatic molecule that contains a charge group onto 30 the carbon cloth material layer which chemical modification of the surface active area may act as an ion exchanger. Azite material consists of micropores which provide superior capacitance properties due to 35 the elimination of one diffusion barrier, that is, macroporous and microporous layers, and is easy to fabricate. Azite material provides for a three dimensional structure and may thus be used alone in connection with merely a non-porous dielectric spacer

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to provide a flow-through capacitor. In addition, since the three dimensional structure of azite is flat with holes, convective flow right through the pores of the material allows a faster method of purification than 5 other materials, such as activated carbon and platinum black, where the porosity is on the surface, and slower processes of electrodiffusion set a limit on the speed of separation.

In one embodiment of a flow-through capacitor of 10 the invention, a spirally wound plurality of layers is adapted to be wound around a hollow central core, the central core acting as the inlet and outlet of the chromatographic column and the central core having a plurality of holes through its length so as to permit 15 the fluid to be separated or purified and to the non-conductive, porous spacer layer in the flow-through capacitor. The flow path may be down through the central layer or from the outside of the flow-through cartridge which is placed in the chromatographic column. Generally, 20 the flow-through capacitor may be sealed at each end and has extending leads which are adapted to be connected to a DC-controlled power supply. The cartridge is formed by rolling up the porous spacer layer, the conductive backing layer, the conductive high surface layer, together 25 with another conductive, porous spacer layer, a second conductive backing layer and the second conductive high surface area layer all about the central tube.

The invention comprises a flow-through capacitor for use in a chromatographic system for the purification 30 of a liquid-containing material.

In another embodiment, the flow-through capacitor of the invention may comprise a plurality of stacked washers or disks secured about a central, non-conductive tube or support means with the washer ends sealed. 35 The central tube means may be porous or have holes punched therein or be a rod having a longitudinal groove(s) for liquid flow.

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The stacked washers comprise in series a first non-conductive spacer washer, for example, of a non-woven, spun-bonded, polymeric, fibrous material, like polypropylene or polyester, a second high surface area conductive washer, for example, a relatively thick layer, e.g. 25 to 200 mils, composed of extruded, activated carbon, conductive polymers, platinum black, compressed bucky balls, etc. and a first conductive backing washer generally a relatively thin, flexible sheet material, e.g. 1 to 5 mils, of graphite foil or a conductive metal, like silver or titanium, on which platinum black is electrodeposited to enhance surface area. Optionally, but preferably, the conductive backing washer has a plurality of holes to permit liquid flow through. The washers are arranged in sequence and stacked about the central tube and secured together in an compressed, contacting arrangements by the pressure of threaded end caps or by threaded rods on each side or by other means. The number of stacked washer units can vary as desired, for example, 10 to 40. Electrical anode and cathode leads from a DC power source are connected to the first and other electrically conductive washers. In one method of connection, notches may be cut in the outside periphery of each conductive backing layer and then opposite rigid electrodes with attending matching tabs secured to each side of the stacked washers with the tabs in electrical contact with the notches of the conductive backing washer.

In another means of electrical connection, the conductive backing washers are made in attached pairs of washers with a short, flexible extension between the washers, so that the extension forms an outwardly extending, bulging, V-shaped, peripheral tab on assembly of the stacked washers, for example, of flexible graphite foil. The electrodes on each side are then placed in contact with the alternate side extending tabs.

The flow-through capacitor may have threaded plastic end caps which are threadably secured to the threaded

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ends of the central tube. The stacked washer flow-through capacitor is then placed within a cartridge holder, such as a standard filter cartridge, with one end of the capacitor sealed by a rubber washer against the 5 outlet of the cartridge. The cartridge would have combination anode and cathode rods, e.g. graphite, extending therethrough and connected to the alternating conductive backing washers. The cartridge includes an inlet for the introduction of a fluid about the 10 capacitor and with the fluid flow from the outside inwardly while subject to a controlled electrical charge. The liquid is then withdrawn from the central tube to the outlet.

The one end of the tab support means may be sealed 15 so that the discharge of purified liquid is from the one open end to the outlet, or the tab supports may be open to each end and each end sealed within the cartridge and purified liquid collected from each end.

The controlled charge chromatography system may 20 be employed for the separation of a wide variety of fluids and more particularly, any solute, solvent or liquid system that wants to be concentrated or purified by resolving into separate species. The solvent can be polar, such as water, or non-polar, such as an 25 aromatic, which fluid contains material which has selectivity for the solid phase and which can be modulated by controlling the charge of the solid phase, that is, the high surface area layer. For example, the solution may be of deionized water with resolved bands of ionic 30 species, such as sodium chloride or other salts, and also any other types of molecules, organic, inorganic or biological. The invention will be disclosed for the purposes of illustration in connection with the separation of ionic liquid solutes; however, the system 35 and method may be advantageously employed and used in the separation of other fluids, such as, but not limited to: non-ionic solutes, like hydrophobic solutes, or other fluids which contain one or more components which

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interact or are affected by electrically conductive surfaces, for example, liquids containing DNA, viruses, bacteria, cells, colloids or mixtures thereof. The flow-through capacitor permits the control of the charge 5 on the stationary phase as the high surface area phase of the flow-through capacitor.

The invention will be described for the purposes of illustration only in connection with certain embodiments; however, it is recognized that those persons 10 skilled in the art may make various modifications, changes, improvements and additions to the preferred embodiments or illustrated embodiments, all without departing from the spirit and scope of the invention.

Brief Description of the Drawings

15 Fig. 1 is an illustrative, schematic, partially exploded view of the flow-through capacitor of the invention;

Fig. 2 is a schematic, illustrative view of the completed flow-through capacitor of the invention;

20 Fig. 3 is a schematic, illustration of a chromatographic column employing the flow-through capacitor of the invention;

Fig. 4 is a schematic illustration of a controlled 25 charge ionic purification chromatography system and method of the invention.

Fig. 5 is a schematic illustrative, exploded view of a stacked washer flow-through capacitor of the invention.

Fig. 6 is a top plan view of the conducting backing 30 washer used in Fig. 5.

Fig. 7 is a perspective view of the assembled flow-through capacitor of Fig. 5.

Fig. 8 is a fragmentary, schematic illustration 35 of a controlled charge chromatographic apparatus of the invention with the flow-through capacitor of Fig. 5.

Description of the Embodiments

With particular reference to Figs. 1 and 2, there is shown in Fig. 1 an exploded view of the flow-through

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capacitor of the invention 10 comprised of a plurality of layers wound about a central plastic tubing 24 having a plurality of perforations 32 therein extending down its length and having a one end which serves an inlet 5 for a fluid to be purified and an other end which serves as an outlet for the discharge of the purified fluid and the ionic species. Layers 12 and 18 which may be the same or different from a non-conductive porous spacer sheet material having a thickness for example of about 10 50 mils to 120 mils, and more particularly, a layer of nylon woven cloth which forms a non-conductive spacer material between the anode and the cathode. Layers 14 and 20 comprise a conductive backing layer which 15 optionally may have holes punched therein to improve flow properties and which may include horizontal leaves extending therefrom to act as leads 28 and 30 for connection to a power source. For example, the conductive backing may comprise Union Carbide's Graphoil® brand 5 mils thick graphite foil with pin holes punched 20 therethrough. Layers 16 and 22 are comprised of a high surface area conductive material, and more particularly in the illustrated embodiment, an activated carbon woven fiber cloth to form a charge-holding, conductive high surface area (for example cloth ANF #62 from Toyobo 25 of Japan).

Fig. 2 is a schematic illustration of the flow-through capacitor wherein the layers have been wrapped around the central core 24 wherein both ends are sealed with an epoxy resin 26 leaving open the inlet 30 of the tube 24 and the outlet. Fig. 2 illustrates a partial sectional view that the inner core tube 24 has a series of holes 32 therein, for example, 16, 1 mm diameter holes, 1/10" apart, on a 3/16" outside diameter tubing as the core. In another embodiment, 35 the capacitor may have no epoxy seals, and a solid tube for a central core, so the flow is between the layers. The capacitor may have the top end of the hollow tube sealed shut so that the direction of flow is through

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the sides of the device, through the successive layers, and then out the open end of the inner hollow tube.

Fig. 3 is an illustration of chromatographic column 34 containing the flow-through capacitor 10 disposed therein and generally axially aligned with the axis of the column 34, the column having an end cap 36, an inlet 38 and connected to a tubing 40 for the introduction of a fluid material to be purified, the end cap gasketed to a defined pressure, for example, 100 psi, and the column 34 having an outlet 42. Extending from the column 34 are the conductive leads 28 and 30 which have epoxy seals where the outlet tubing 50 and the Graphoil leads 28 and 30 come through column 34. For example, the column 34 may comprise a transparent, plastic, polypropylene, syringe-type barrel.

Fig. 4 is a schematic illustration of a controlled charge purification chromatography system and includes a source of fluid, such as a solution source 46, inlet tubing 40 which passes through a pump 48 to connect the fluid into the inlet 38 of the end cap 36 of the chromatographic column 34 which contains the flow-through capacitor 10 wherein the leads 28 and 30 from the capacitor 10 are connected to an electric control system 56 which programs and controls the voltage, the off/on cycles, voltage gradients and permits reversal of polarity and otherwise controls the electric power to the flow-through capacitor through a 24-volt DC power supply 58. The outlet from the column 34 is through outlet 42 through a tube 50 which directs the material or the elution to a rotating-type fraction collector schematically illustrated as 52. The outlet 42 may have an on/off fluid control valve.

The chromatographic system as illustrated in Fig. 4 may be employed to provide for the purification of a variety of solutions containing ionic material, and for example, the purification of a 0.01 molar sodium chloride aqueous solution from feed 46 which is fed by pump 48 through tubing 40 into the inlet 38 of the

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end 36 to the column 34 and hence, through 24 into the flow-through capacitor 10 which has a controlled charge thereon of about 2 volts. The sodium chloride feed solution is purified to a 1×10^{-4} molar at a flow rate 5 of .23 ml/minute from the outlet 42 through control valve 60 into the tubing 50 into the fraction collector 52, while 2 volts are also supplied to the DC power supply through logic 56 to leads 28 and 30 to provide a flow-through capacitor. The purified sodium chloride 10 solution was recovered simply by shorting the leads 28 and 30. In other examples, much larger peak or outlet was obtained from a 5×10^{-4} purified outlet to a 0.05molar outlet peak by reversing the polarity of the leads 28 and 30 for about 5 seconds. The flow rates may vary; 15 however in purification experiments with sodium chloride, the flow rates vary from 0.23 ml per minute to 3 ml per minute or more.

Fig. 5 shows a stacked washer flow-through capacitor 100 in an exploded form having a rubber washer 102 at 20 the top end thereof to form a watertight seal when the capacitor 100 is put inside a standard filter cartridge holder 126 (see Fig. 8). The cartridge 100 contains end caps 106 made of an inert, non-conductive material, such as for example a high density polypropylene resin, 25 with the end caps threaded on the inside to screw onto threads 108 on the end of a central tube 110. The bottom end cap 106 is a solid cap to close up the bottom end of the tube 110. The top end cap includes two concentric circles of inert conductive material 104, such as for example, but not limited to, gold, gold-foil, graphite or platinum series metals and the like. The central supporting tube 110 comprises a porous polyethylene tube, for example a 10-inch tube of porous plastic with a 3/8-inch outside diameter and 1/8-inch wall thickness. 30 The central tube 110 acts as a supporting member to hold the ring-shaped or washer parts together and under compression when the end caps 106 are threadably screwed against the ends of the central tube 110. The porous 35

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plastic tube 110 allows for flow out of the middle of the tube to the top end. The tube could also include a solid, rod-like element with longitudinal, fluted sides to provide support for the washer elements and 5 also provide for flow out of the tube. Employment of a central, plastic, porous, polyethylene tube has the added advantage of being also a microfilter, for example, of one to five microns or less, so as to filter out any fine material which may leach off a carbon disk 10 or other washer materials. The cartridge 100 includes a plurality of washer materials in sequence to include a porous, non-conductive spacer material with pores, for example, a synthetic, fibrous material or other type of non-conductive spacer material, such as fiberglass 15 or woven nylon.

Washer material 116 comprises any inert, conductive backing material, for example, a 5-mil thick Graphoil® brand (Union Carbide graphite foil material) with multiple holes 119 perforated in it to provide for better liquid 20 flow therethrough. This graphite foil material (also see Fig. 6) provides a pair of washer materials 116 connected with a connecting bridge 118 having an optional notch 114 to accommodate electrical communication to a conductive material. The conductive material 116 25 with the connecting tab 118 is placed at the top and bottom of a high surface area conductive washer material 120 with half the resistance to an average particle in the conductor 120 thereby providing a capacitor with less internal resistance, which is desirable, as it 30 increases the speed with which the capacitor may be electrically charged, and therefore the allowable flow rate of the solution to be purified can be increased. The tab or arm 118 connecting the two halves of the backing material 116 provides for the connecting tab 35 or arm 116 to be crimped to form tabs that extend outside of the completed assembled flow-through cartridge, which tabs can then be utilized to form conductive leads. In one preferred embodiment, the conductive leads having charge may be faced inwardly.

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The washer material 120 comprises any high surface area conductive material. One example is the use of a KX Industries extruded, activated carbon tubes which are held together with a small amount of polypropylene binder. These tubes are extruded in tube shapes two inches overall diameter with an inner diameter which is widened to 1-3/8 inches and cut into rings of about 1/8 inch thickness. Such high surface area conductive material 120 may also include activated carbon cloth full of activated carbon fibers, since the compression afforded by the stacked washer cartridge flow design would compress the loose material and allow it to become conductive by inner particle contact, thus allowing the choice of other inexpensive, conductive, high surface area conductive materials.

The conductive leads material 122, as shown on the right hand side of the exploded diagram in Fig. 5, includes folded tabs 124 which can be made of any electrically conductive material, such as for example Graphoil®, or may also be a wire suitably coated to protect it from the environment or a naked inner wire of gold or platinum, along with the electrically conductive material, could be attached to the arm 118. The conductive material as illustrated is shown in corrugated form. The flat tab section 124 is designed to lie on top of parts 120 or 116 to form an electrical contact under compression. As illustrated, an option notch 114 can be employed to accommodate thickness of the tab, while in many cases the other materials are compressible enough so this added notch need not be employed. The conductive leads 122 and tabs 124 short together the alternating layers composed of conducting layers 116 and 120 which are separated by the insulating spacer 112 to form alternating washer anodes and cathodes up and down the central tube 110.

Fig. 7 shows the assembled flow-through capacitor cartridge 100 showing the side leads 122 that short the alternating anode and cathode washer layers together

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in parallel. The tabs 124 are now pressed against the backing layers 116 to form electrical contact. The conductive leads 122 are also electrically connected on each of the conducting circles 104 in the end cap 5 106. The assembled flow-through capacitor cartridge 100 as illustrated in Fig. 7 is thus ready for insertion in a standard filter cartridge for use as a controlled charge chromatography system.

Fig. 8 is a fragmentary, partially sectional, 10 schematic illustration of a controlled charge chromatography apparatus showing the use of the flow-through capacitor cartridge 100 within a standard filter cartridge 126 having a screw-on head 128 with the inlet 130 for the introduction of a liquid for a 15 controlled charge chromatographic separation, and an outlet 132 for the removal of a purified liquid from the center of the central supporting tube 110. The cartridge head 128 is modified to allow watertight, 20 electrically conductive leads 138 to an outside DC power supply (not shown) with the employment of paired conductive rods, for example 3/8-inch graphite rods 134 and 136, having pointed ends, which are in electrical contact with the concentric circles 104 and the end caps 106 of the cartridge 100, with compression nuts 25 used to form a watertight seal over the rods 134 and 136. Threaded inserts go in to the filter holder cartridge top 128 to corresponding threaded holes in the top cover for the employment of the rods 134 and 136 in a watertight fashion. The rods have leads 138 30 to a power supply (not shown by see Fig. 4). The filter holder top 128 is screwed tightly to form a watertight seal against washer 102. The conductive rods 134 and 136 are pressed firmly against the concentric conducting circles 104, thereby forming electrical contact through 35 to the leads 122. Since the washers are concentric, no matter how the top is screwed on, the rods 134 and 136 will always be positioned in the right place against conductive circles 104.

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In operation, a liquid to be purified is introduced through inlet 130, 130 flows to the outside within cartridge 126, and goes through from the inside to the outside of the washer 102. Purified fluid is then removed 5 through the central tube 110 and therefore through outlet 132. While the conductive backing material has been described in a particular form, that is, two washers 116 with a conducting arm bridge 118, this particular form is not essential to the operation of the flow-through 10 capacitor of the invention, and obviously may be replaced by other forms, but the illustrated form represents one preferred embodiment employing the electrically conductive backing material in the stacked washer flow-through capacitor of the invention.

15 Thus, as illustrated a new, improved and unique flow-through capacitor and controlled charge purification chromatography column system and method has been discovered which provides for the effective and rapid separation by a flow-through capacitor of high electric 20 capacitance and high surface area, high adsorption ability, electrically conductive, stationary phase in the chromatographic column.

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- 15 4 Strohl, John and Polutanovich, Thomas, "A Packed Graphite Cell for Thin-Layer Chromatography", Analytical Letters, 2(8), pp. 423-431 (1969)
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- 8 Newman, Arnold L., "Sintered Pellet with Biochemically Active Layer", U.S. Patent 4,769,191, September 6, 1988
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CLAIMS

What is claimed is:

Claim 1. A flow-through capacitor for use in a controlled charge chromatographic column for the purification of liquids, which flow-through capacitor comprises:

- a) a plurality of adjacent layers of a first spacer layer, a first backing layer, a first surface area layer, a second spacer layer, a second backing layer and a second surface area layer, the first and second spacer layers comprising an electrical, non-conductive, porous spacer layer to permit the flow of liquid therethrough; said first and second backing layers comprising a first and second electrically conductive backing layer; said first and second surface area layers comprising a high surface area electrically conductive layer to act as the stationary phase of a chromatographic column, said layers being sized, dimensioned and positioned to allow for placement onto a chromatographic column;
- b) an anode and a cathode lead extending from the first and second backing layers, which anode and cathode leads are adapted to be connected to a DC power source to provide separate and opposite electrical charges on the first and second backing layers;
- c) a central, porous tube positioned to permit the flow of a liquid to be purified through the plurality of adjacent layers;
- d) means to seal the tube and the adjacent layers; and
- e) means to introduce or withdraw a liquid into or from the central tube.

Claim 2. The capacitor of claim 1 wherein the non-conductive, porous spacer layer comprises a synthetic, open fiber material.

Claim 3. The capacitor of claim 1 wherein the electrically conductive backing layer comprises a

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4 conductive film layer selected from a group consisting
of: aluminum, tantalum and graphite.

2 Claim 4. The capacitor of claim 1 wherein the
high surface area conductive layer comprises compressed,
activated carbon particles.

2 Claim 5. The capacitor of claim 1 wherein the
high surface area conductive layer comprises activated
carbon woven fibers.

2 Claim 6. The capacitor of claim 1 wherein the
high surface area conductive layer comprises
electrodeposited platinum series black.

2 Claim 7. The capacitor of claim 1 wherein the
first and second backing layers have holes therein for
the flow of liquid therethrough.

2 Claim 8. The capacitor of claim 1 wherein the
plurality of adjacent layers are arranged in spiral
wound form about the central tube.

2 Claim 9. The capacitor of claim 1 wherein the
plurality of adjacent layers are arranged as stacked
washer elements about the central tube.

2 Claim 10. The capacitor of claim 9 wherein the
washer elements are connected by an electrically
conductive tab.

2 Claim 11. The capacitor of claim 10 wherein the
washer elements comprise a graphite foil material.

2 Claim 12. A chromatographic column for the
purification of liquids, which column includes therein
the flow-through capacitor of claim 1.

2 Claim 13. A method for the controlled charge
chromatographic purification of a fluid, which method
comprises:

4 a) introducing a fluid having materials to be
removed into the inlet of a cartridge containing
6 a flow-through capacitor of claim 1, the anode
and cathode elements electrically connected to
8 a power supply to provide controlled charge anode
and cathode layers in the capacitor;

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- 10 b) passing the fluid to be purified through the
12 high surface area layers to permit the controlled
14 charge absorption of one or more materials in the
 fluid onto the surface area layers; and
 c) discharging a chromatographically purified
 fluid from an outlet in the cartridge.

Claim 14. The method of claim 13 wherein the fluid
2 comprises an aqueous solution containing one or more
4 ionic salts therein to provide a purified aqueous solution
 with the removal of one or more of the ionic salts.

AMENDED CLAIMS

[received by the International Bureau on 27 April 1993 (27.04.93) ;
original claims 1,2,8-16 amended; other claims unchanged (3 pages)]

What is claimed is:

Claim 1. A flow-through capacitor for use in a
2 controlled charge chromatographic column for the
purification of liquids, which flow-through capacitor
4 comprises:

- a) a plurality of adjacent layers of a first spacer
6 layer, a first backing layer, a first surface area
8 layer, a second spacer layer, a second backing layer
10 and a second surface area layer, the first and second
12 spacer layers comprising an electrical, non-conductive,
14 porous spacer layer to permit the flow of liquid
therethrough; said first and second backing layers
16 comprising a first and second electrically conductive
18 backing layer; said first and second surface area
layers comprising a high surface area electrically
20 conductive layer to act as the stationary phase of a
22 chromatographic column, said layers being sized,
24 dimensioned and positioned to allow for placement onto
26 a chromatographic column;
- b) an anode and a cathode lead extending from the
28 first and second backing layers, which anode and
cathode leads are adapted to be connected to a DC power
30 source to provide separate and opposite electrical
charges on the first and second backing layers;
- c) a central, support means positioned to permit the
flow of a liquid to be purified through the plurality
32 of adjacent layers;
- d) means to seal the support means and the adjacent
34 layers within a column; and
- e) means to introduce or withdraw a liquid into or
36 from the central tube.

Claim 2. The capacitor of claim 1 wherein the non-
2 conductive, porous spacer layer comprises a synthetic, fiber
material.

Claim 3. The capacitor of claim 1 wherein the
2 electrically conductive backing layer comprises a conductive
4 film layer selected from a group consisting of: aluminum,
tantalum and graphite.

Claim 4. The capacitor of claim 1 wherein the high 2 surface area conductive layer comprises compressed, activated carbon particles.

Claim 5. The capacitor of claim 1 wherein the high 2 surface area conductive layer comprises activated carbon woven fibers.

Claim 6. The capacitor of claim 1 wherein the high 2 surface area conductive layer comprises electrodeposited platinum series black.

Claim 7. The capacitor of claim 1 wherein the first 2 and second backing layers have holes therein for the flow of liquid therethrough.

Claim 8. The capacitor of claim 1 wherein the 2 plurality of adjacent layers are arranged in spiral wound form about the central support means.

Claim 9. The capacitor of claim 1 wherein the 2 plurality of adjacent layers are arranged as stacked washer elements about the central support means.

Claim 10. The capacitor of claim 9 wherein the washer 2 elements are arranged in pairs and are connected by an electrically conductive tab.

Claim 11. The capacitor of claim 10 wherein the pairs 2 of washer elements comprise a graphite foil material.

Claim 12. The capacitor of claim 1 wherein the central 2 support means comprises a porous or perforated plastic tube.

Claim 13. The capacitor of claim 1 wherein the central 2 support means comprises a rod having longitudinal grooves for liquid flow.

Claim 14. A chromatographic column for the purification 2 of liquids, which column includes therein the flow-through capacitor of claim 1.

Claim 15. A method for the controlled charge 2 chromatographic purification of a fluid, which method comprises:

4 a) introducing a fluid having materials to be removed
into the inlet of a cartridge containing a flow-through
6 capacitor of claim 1, the anode and cathode elements
electrically connected to a power supply to provide

8 controlled charge anode and cathode layers in the
capacitor;
10 b) passing the fluid to be purified through the high
surface area layers to permit the controlled charge
12 absorption of one or more materials in the fluid onto
the surface area layers; and
14 c) discharging a chromatographically purified fluid
from an outlet in the cartridge.

Claim 16. The method of claim 15 wherein the fluid
2 comprises an aqueous solution containing one or more ionic
salts therein to provide a purified aqueous solution with
4 the removal of one or more of the ionic salts.

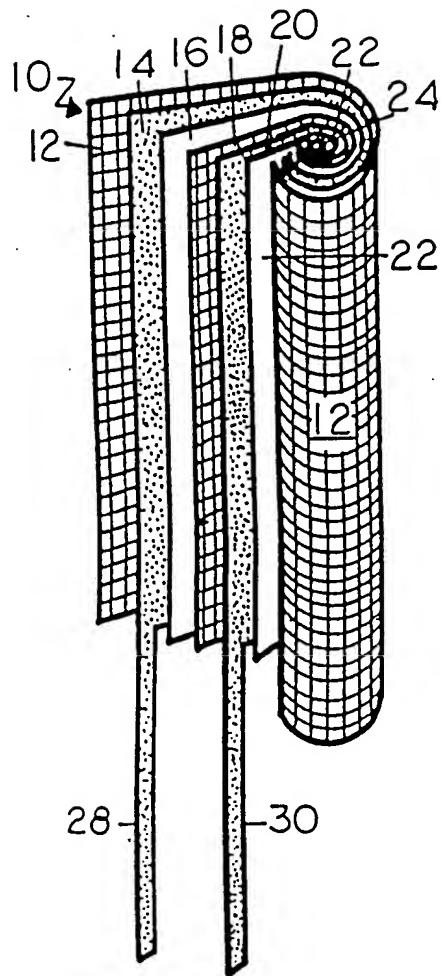


FIG. 1

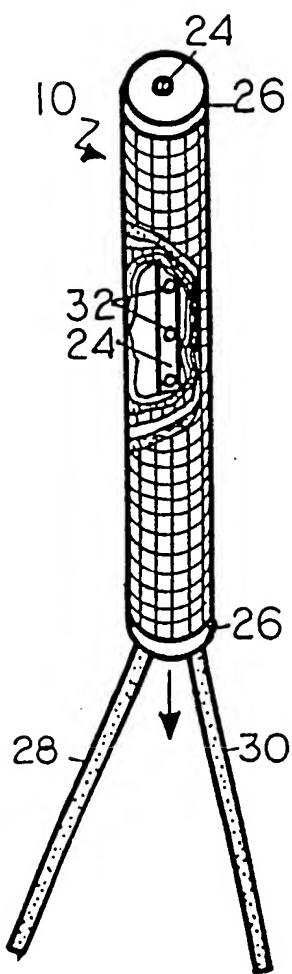


FIG. 2

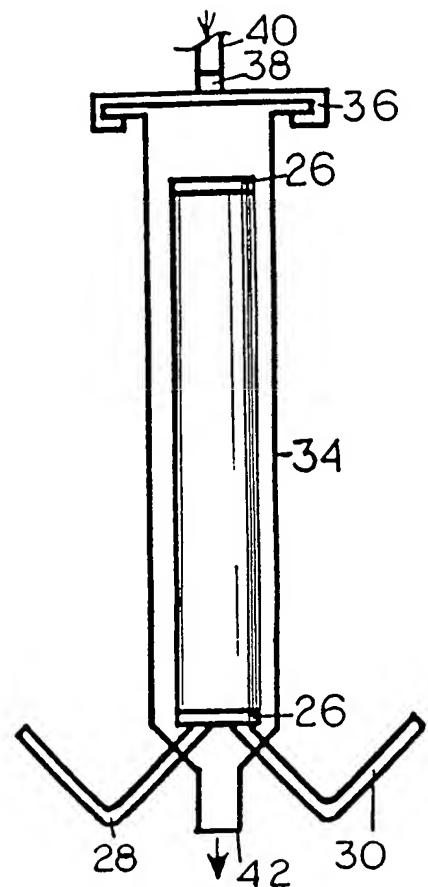


FIG. 3

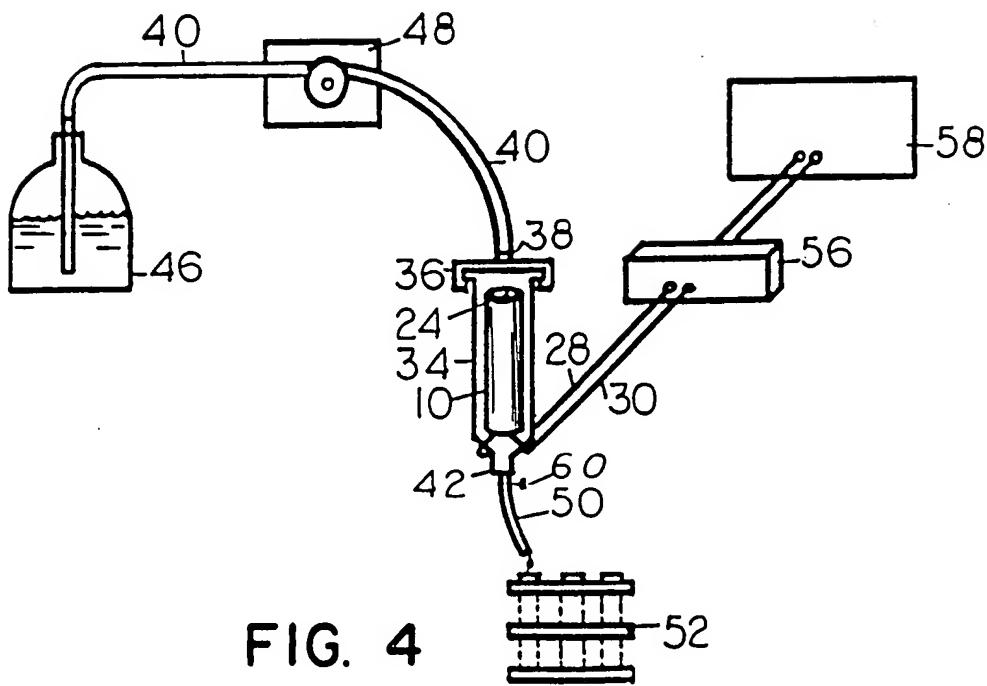
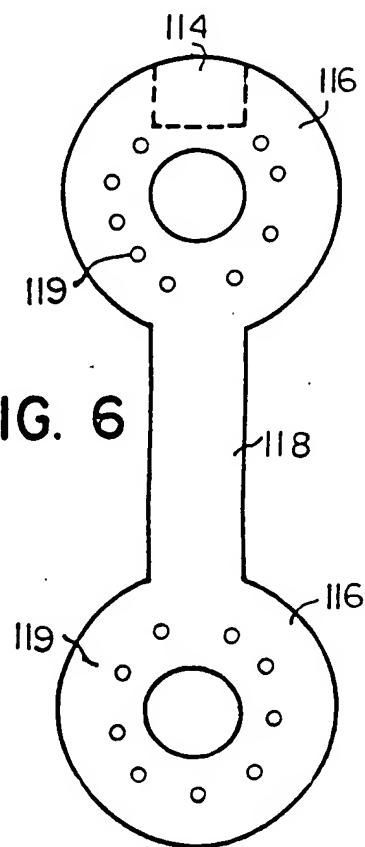
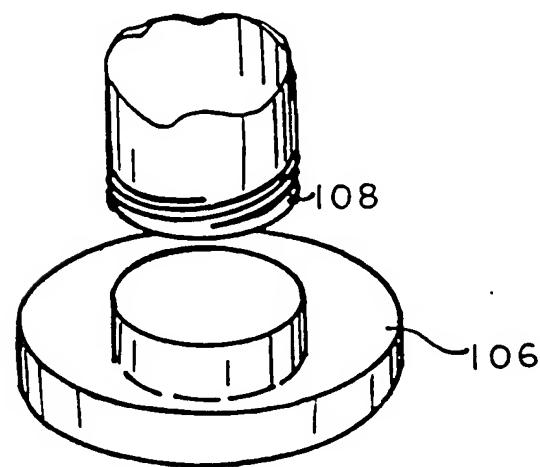
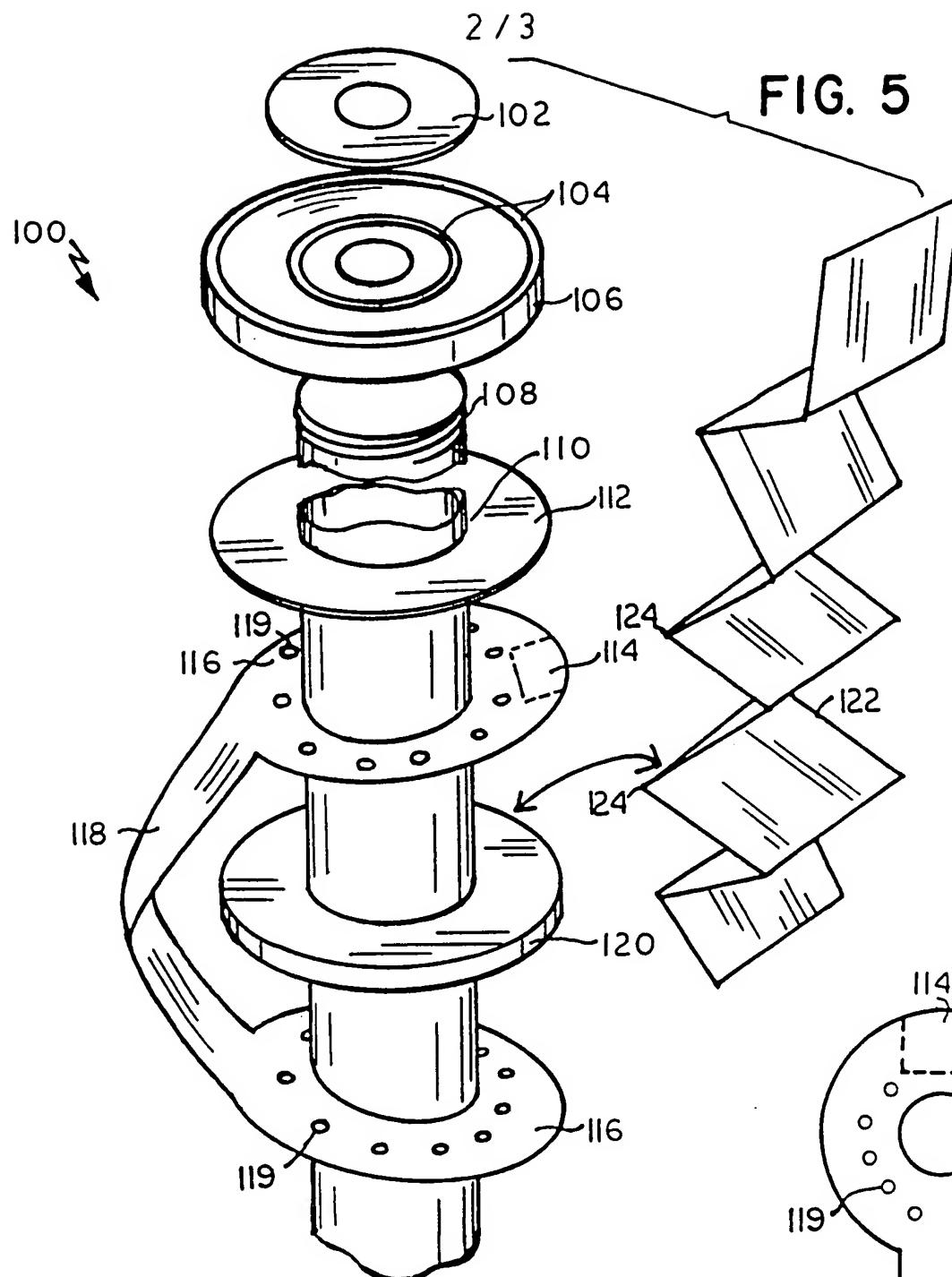


FIG. 4



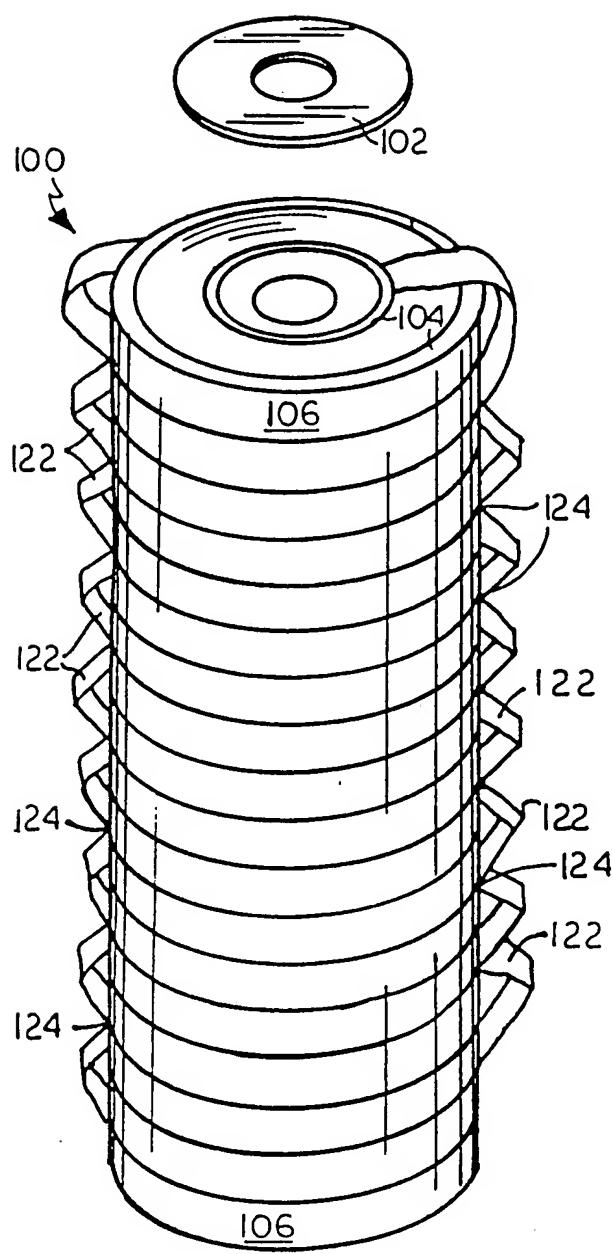


FIG. 7

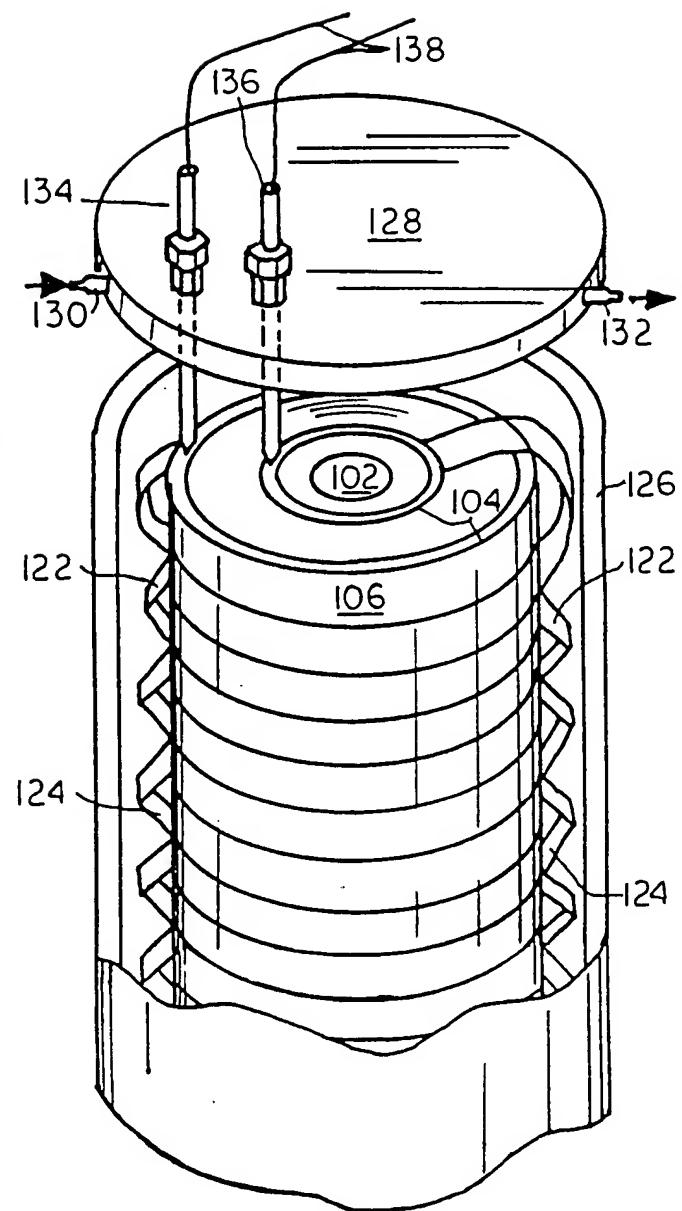


FIG. 8

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B01D 15/08

US CL :210/656,198.2

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 210/243,541,635,747; 204/180.1,299R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BASSLER, BARBARA and HARTWICK, RICHARD A., "Electrically Conductive Stationary Phases for HPLC", Abstract #179B from AICHE Annual Meeting in San Francisco, Ca. on November 5-10, 1989. See column 1, lines 1-5.	1-14

Further documents are listed in the continuation of Box C.

See patent family annex.

•	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
•A	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
•E	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
•L	document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
•O	document referring to an oral disclosure, use, exhibition or other means		
•P	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

10 FEBRUARY 1993

Date of mailing of the international search report

10 FEBRUARY 1993

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